$$E_n^{(1)} = \langle \psi_n^{(0)} | z | \psi_n^{(0)} \rangle$$
$$= 0$$

Lecture 13

Note that atomic states $|\psi_n^{(0)}\rangle$ are eigenstates of parity.

This is because $\mathcal{P}\vec{x}\mathcal{P}^\dagger = -\vec{x}$ & $\mathcal{P}\vec{p}\mathcal{P}^\dagger = -\vec{p}$

but H_0 involves only $|\vec{p}|^2$ & $1/|\vec{x}| \equiv 1/r$

Thus $[H_0, \mathcal{P}] = 0$ or $\mathcal{P}H_0\mathcal{P}^\dagger = H_0$

Thus $|\psi_n^{(0)}\rangle$ are also eigenstates of $\mathcal{P}$.

Then consider

$$\langle \psi_n^{(0)} | z | \psi_n^{(0)} \rangle$$

$$= \langle \psi_n^{(0)} | \underbrace{\mathcal{P}^\dagger \mathcal{P}}_{\mathbb{1}} z \underbrace{\mathcal{P}^\dagger \mathcal{P}}_{\mathbb{1}} | \psi_n^{(0)} \rangle$$

Then use the facts that

$$\mathcal{P} z \mathcal{P}^\dagger = -z \qquad \& \qquad \mathcal{P} | \psi_n^{(0)} \rangle = \pm | \psi_n^{(0)} \rangle$$

(Recall $\mathcal{P}\mathcal{P}^\dagger = \mathbb{1}$; $\mathcal{P} = \mathcal{P}^\dagger$ i.e $\mathcal{P}^2 = \mathbb{1}$
thus $\mathcal{P}$ eigenvalues are ± 1)

Thus $\langle \psi_n^{(0)} | z | \psi_n^{(0)} \rangle = - \langle \psi_n^{(0)} | z | \psi_n^{(0)} \rangle$ i.e. $= 0$

In the next order, let us consider the ground state

$$E_1^{(2)} = \sum{}' e^2|\vec{E}|^2 \frac{|\langle\psi_k^{(0)}|z|\psi_1^{(0)}\rangle|^2}{E_1^{(0)} - E_k^{(0)}}$$

Note again that from $\psi_k^{(0)}$ states, ~~only~~ in the notation $|n, \ell, m\rangle$ only $\ell = 1$ states contribute i.e. $\langle n, \ell, m| z |1, 0, 0\rangle \propto \delta_{\ell 1}\, \delta_{m0}$

This can be checked in two ways:

1. Use $\mathcal{P}|n, \ell, m\rangle = (-1)^{\ell}|n, \ell, m\rangle$ & $|m\rangle \sim e^{im\phi}$ $\quad \langle m|m'\rangle \sim \int d\phi\, e^{-im\phi + im'\phi}\, d\phi$

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Also recall $z = r\cos\theta$ $\sim P_1(\cos\theta)$

$l=0:$ $P_0(\cos\theta) = \text{const.}$ $\quad l=1:$ $P_{l=1}(\cos\theta) \sim \cos\theta$

$$\int d(\cos\theta)\, P_l(\cos\theta)\, z\, P_{l'=0}(\cos\theta)$$

$$\sim \int d(\cos\theta)\, P_l(\cos\theta)\, P_1(\cos\theta) \propto \delta_{l1}$$

Regardless of above comments, a crude estimate for $E_1^{(2)}$ is possible by observing

1) Let all denominators be replaced by the smallest value $E_1^{(0)} - E_2^{(0)}$

2) Then the numerator can be summed

$$\sum_k{}' |\langle \psi_k^{(0)} | z | \psi_1^{(0)} \rangle|^2$$

$$= \sum_k{}' \langle \psi_1^{(0)} | z | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | z | \psi_1^{(0)} \rangle$$

The restriction $k \neq 1$ can be dropped

$\because \langle \psi_1^{(0)} | z | \psi_1^{(0)} \rangle = 0$

$$= \sum_k \langle \psi_1^{(0)} | z | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | z | \psi_1^{(0)} \rangle$$

$$= \langle \psi_1^{(0)} | z^2 | \psi_1^{(0)} \rangle$$

Further this is $\frac{1}{3} \langle \psi_1^{(0)} | r^2 | \psi_1^{(0)} \rangle$

which can be calculated to be a_0^2

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~~Thus~~, next use

$$-E_1^{(0)} + E_k^{(0)} \geq -E_1^{(0)} + E_2^{(0)}$$

$\underbrace{}_{\text{g.s.}}$

$$= -\frac{e^2}{2a_0}\left(1-\frac{1}{4}\right)$$

$$-E_1^{(2)} \stackrel{e^2|\vec{E}|^2}{=} \cancel{\frac{4}{3}}\, a_0^2 \times \frac{2a_0}{e^2} \times \frac{4}{3} = \frac{8}{3\cancel{e^2}} a_0^3 \cdot \cancel{e^2} |\vec{E}|^2$$

Experimentally, polarisability α is defined as $\alpha = -\dfrac{\partial^2 (\Delta E)}{\partial |\vec{E}|^2} = +\dfrac{16}{3} a_0^3$

Stark effect (linear)

(Example of deg. pert. th.)

We consider H atom

Study the effect of $V = -ez|\vec{E}|$

on the $n=2$ levels

$n=2$; $m_\ell = 0$ & $m_\ell = -1, 0, 1$

s level   p level

Only $\ell=0, m=0$ & $\ell=1, m=0$ states mix

Prescription for deg. pert. theory:

- Diagonalise matrix $V\!\!/$ which is $\langle k_1^{(0)} | V | k_2^{(0)} \rangle$ evaluated within the degenerate subspace D

Here

$$
V\!\!/ = \begin{array}{c}
\begin{array}{cccc} 0,0 & 1,0 & 1\,\text{-}1 & 1\,1 \end{array} \quad l, m \\
\left(\begin{array}{cc|cc} 0 & \Delta & 0 & 0 \\ \Delta & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array} \right)
\end{array}
$$

Calculate $\langle 2,0,0 | z | 2,1,0 \rangle = -3a_0$

Eigenvalue prob: $\det \begin{vmatrix} 0-\lambda & -3a_0 \\ -3a_0 & 0-\lambda \end{vmatrix} = 0 \Rightarrow \lambda = \pm 3a_0$